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Physical Properties of Sprayed Sn2S3 Nanocrystalline Thin Films

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Abstract- Sn_2S_3 films were prepared on glass substrate by spray pyrolysis method at 270 °C. The optical constants and thickness of the films were extracted using the pattern search optimization technique in combination with a seed preprocessing procedure. The porosity was deduced by using effective medium approximation EMA. Refractive- index dispersion of the films was analyzed using the concept of the single oscillator model. The values of the oscillator energy, $E_{0,}$ and the dispersion energy, $E_{d,}$ were determined as 13.5 eV and 3.99 eV, respectively. Using the semi empirical model of Wemple and DiDomenico, the parameter β has been estimated to be 0.22, which indicated that Sn_2S_3 film falls into ionic class. The analysis of the optical properties of the Sn_2S_3 film showed an indirect and direct transition with energys gap 0.74 eV and 2 eV, respectively. The materials properties such as dielectric constants, effective mass, carrier concentration and plasma frequency were also evaluated.

Keywords**:** *Thin film, optical properties, Single-oscillator model.*

I. INTRODUCTION

In the last few years, compounds based on the Sn-S system have attracted considerable attention due to their potential application in photovoltaic devices and near-infrared (NIR) detectors. In addition, elements Sn and S are abundant in nature and they do not contribute too pollution during the deposition. Several binary compounds based on the Sn-S system are known (SnS, Sn_2S, Sn_2S_3, Sn_3S_4, and Sn_4S), of which SnS, Sn_2S and Sn_3S_3 are the most important.

In Sn_2S_3, tin atoms [Sn(II) and Sn(IV)] and three sulfur atoms [S(1), S(2) and S(3)] occupy five different 4c positions in the orthorhombic space group Pnma . The crystal structure of Sn_2S_3 is tetragonal composed of Sn_2S_3 chains, with the Sn(IV) ions adopting chain center position with octahedral coordination to S, and the Sn(II) ions adopting chain-end position in the favored trigonal-pyramidal arrangement. The Sn_2S_3 compound is classified as a mixed valence compound with semiconducteur behavior and exhibits n-type conductivity having band gap 0.9- 2.2 eV [1-4] whose optoelectronic properties are dependent on its crystalline structure and stoichiometry. This material appears to be suitable for preparing near-lattice-matched hetero-junctions in systems like Sn_2S_3/CdTe, Sn_2S_3/GaSb, Sn_2S_3/AlSb, etc. These systems have applications in the detection and generation of infrared radiation.

In this work the optical constants of nanocrystalline Sn_2S_3 thin film were fitted in terms of the Lorentz multiple oscillator model by using the pattern search technique in combination with a seed preprocessing procedure spSP. The analysis of the optical properties was conducted by single oscillator model by defining a dispersion energy parameter E_d. Also, dielectric constant, effective mass and carrier concentration were determined.

II. EXPERIMENTAL DETAILS

As previously reported [2], Sn_2S_3 thin films have been deposited at substrate temperature of 270 °C by Spray pyrolysis technique. The starting chemical solution was prepared using 0.1 N pure tin chloride ($SnCl_2$) and Thiourea ($CS(NH_2)_2$). The prepared solutions of tin chloride and thiourea were appropriately mixed to obtain Sn:S proportion of 2:3. The obtained solution was pulverised on glass substrates with compressed air (2 bars) and at flow rate of 8ml/min. The distance from the spray nozzle to the heater is kept approximately at 29 cm. Under these deposition conditions, good films were obtained. They were uniform and very adherent to the substrates. Structural characterization has been carried out at room temperature using a Philips 1830 X-ray diffractometer with a C_uK_α peak λ=1.546Å. The optical transmittance and reflectance were recorded from 200 to 2500 nm wavelength using an UV (Ultra-Violet) Visible JASCO type V-570 double beam spectrophotometer. Morphology was carried out by a Joel JSM 5800 scanning electron microscope.

III. RESULTS AND DISCUSSION

Figure.1 demonstrates the X-ray diffraction pattern of nanocystalline Sn_2S_3 thin film deposited on glass substrates according to the experimental conditions mentioned previously. The all peaks were indexed in according the experimental ASTM X-ray powder data files (Card No. 17- 0031). The grain size (G) of nanocrystallite has been estimated from Scherrer formula [5], using the full- width at half –maximum of the more intense diffraction peak. Then the diameter D of nano-crystallite is given by ($D = \frac{4G}{3}$). The determined value of the grain size from the peak (211) is equal to 130 Å. Figure. 2 shows the scanning electron micrograph of Sn_2S_3 thin film. It was observed that film was homogenous and was of nanocrystalline nature. The grains were approximately spherical in shape and were uniformly distributed over the substrate without any cracks.

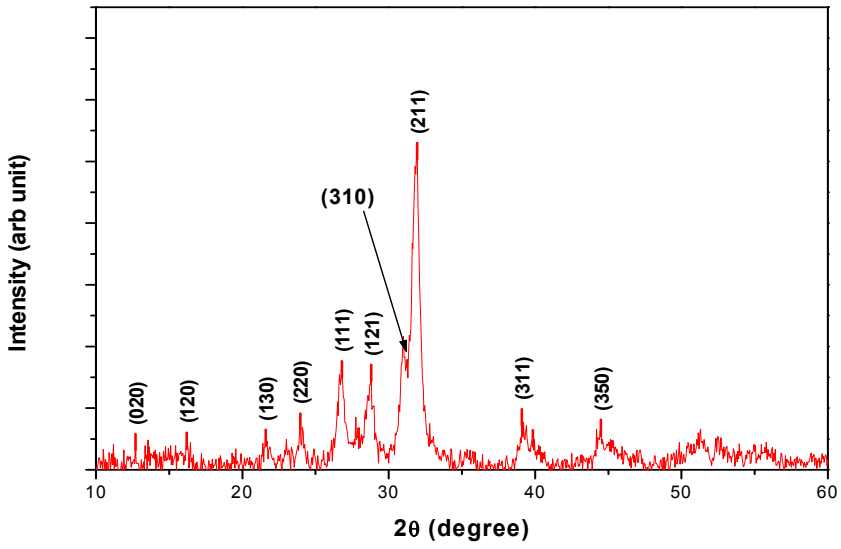

Figure. 1. *Experimental X-ray diffraction patterns of Sn_2S_3 prepared by spray pyrolysis method.*

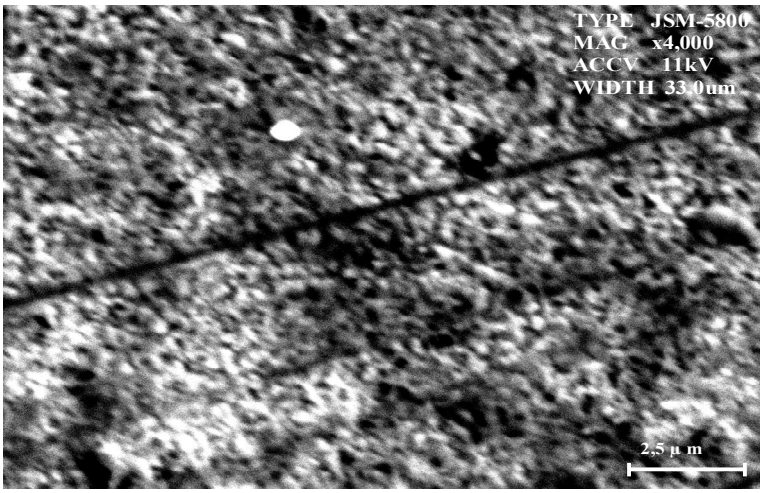

Figure. 2. *SEM image of Sn_2S_3 nanocrystalline thin film deposited at 270 ° C.*

The optical constants (n, k) and the thickness (d) were obtained with the spPS (seed preprocessing Pattern search) technique [6]. The fitted refractive index and extinction coefficient are plotted in Figure. 3. Fitting of the optical constants has been done using a Lorentez multiple oscillator models. The layer thickness and surface roughness are found to be 130 nm and 15 nm, respectively. The refractive index and extinctive coefficient monotonically change until a critical wavelength λ_c = 600 nm wich is close to the wavelength corresponding to the optical energy band gap. In particular, the refractive index and extinctive coefficient value at λ=800 nm are approximately 1.96 and 0.08, respectively, which is in agreement with the reported values of N.K. Reddy et al. [7]. In order to estimate the band gap energy of the Sn_2S_3 thin film, the single-oscillator model proposed by Wemple and DiDomenco [8] was used to formalize the dispersion function in the visible region, this model is given by the expression:

$$n^2 - 1 = {E_0 E_d}\Big/{(E_0{}^2 - E^2)} \quad (1)$$

where n is refractive index, E0 is the energy of effective dispersion oscillator, E is the photon energy, and Ed is the dispersion energy. E0 and Ed have a significant association with the crystalline structure and ionicity of ionic or covalent materials. The values of Ed and E0 are obtained from the intercept and slope resulting from the extrapolation of the curve of Figure. 4 as 13.5 and 3.99 eV, respectively. The value of the refractive index at the IR wavelength was n = 2.09. This value was significantly lower than that of bulk Sn2S3 materials (n = 2.9) [9]. The difference between the two indices is generally interpreted as a consequence of the presence of void inclusions in the layer. From these we estimated the porosity p = 36 %, by using the Bruggeman effective medium approximation (EMA) model [10].

As was shown by Tanaka [11], the oscillator energy E_0 scales with the energy gap very well, according to the expression $E_g^d \approx E_0/2$. Hence, we found that the optical band gap energy $E_g \approx 1.99\ eV$, this value is in good agreement with what was found ($E_g \approx 2\ eV$) in our previous work [3].

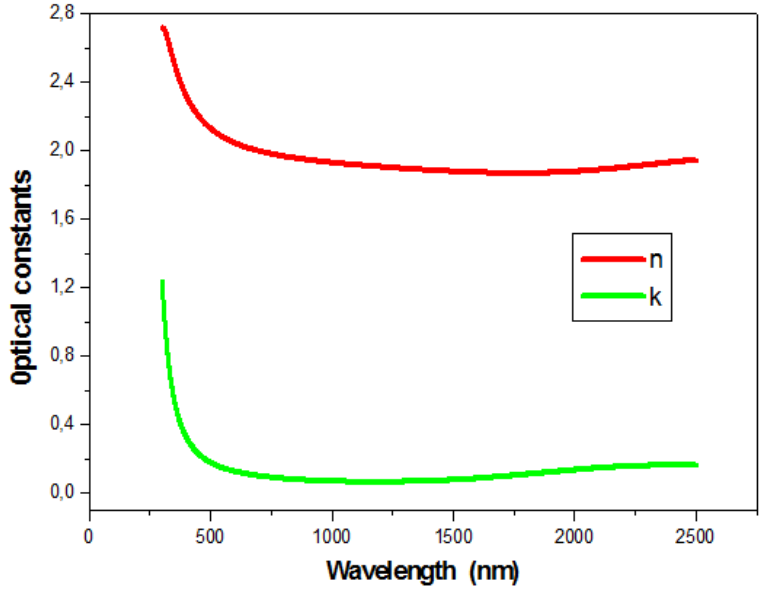

Figure. 3. *Refractive index and extinction coefficient from fitting of a two-term Lorentz dispersion equation.*

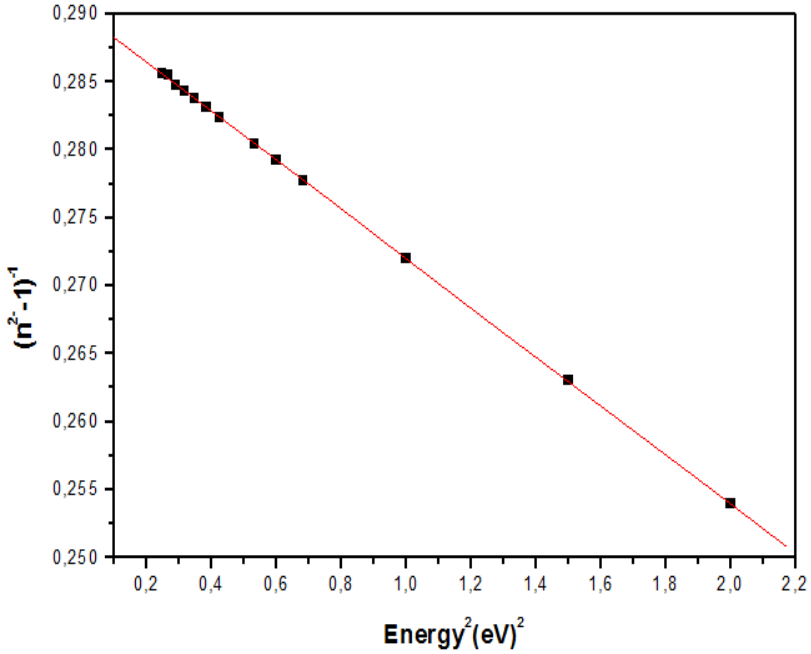

Figure.4. *Plots of $(n^2\text{-}1)^{-1}$ versus E^2 of Sn_2S_3 thin film.*

The indirect optical transitions in crystalline semiconductors can be extracted from the energy dependence of the imaginary part of the dielectric constant ε_2 via the following relation [12]:

$$\varepsilon_2(E) = \frac{D}{E^2}\left(E - E_g^{ind}\right)^2 \theta\left(1 - \frac{E_g^{ind}}{E}\right)\theta\left(1 - \frac{E}{E_c}\right) \qquad (2)$$

where $E = h\gamma$, D is a nondimensional strength parameter, E_c is a higher energy cut off and θ is Heaviside function given by :

$\theta(Z) = 1$ for $Z \geq 0$ and

$\theta(Z) = O$ for $Z < 0$ (3)

E_g^{ind} is the indirect optical transition. In Figure.5 we plot $E\varepsilon_2 (E)^{1/2}$ versus photon energy E for Sn_2S_3 thin film. The indirect gap energy is found to be 0.74 eV, this value is in good agreement with the values reported for Sn_2S_3 [13-14].

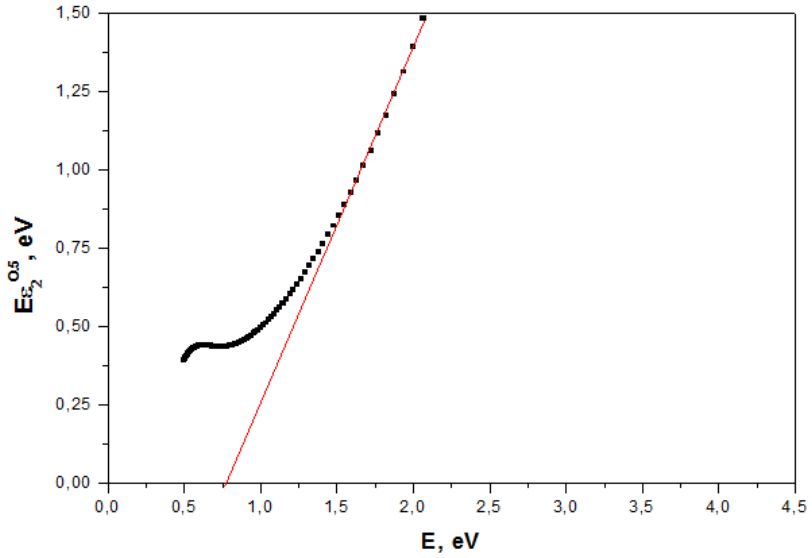

Figure.5. *Plots of $E\varepsilon^{0.5}(E)$ versus E of Sn_2S_3 thin film.*

The dispersion energy, E_d, describes the dispersion of the electronic dielectric constant and it is related to interband transition strength. Ed is found to obey an empirical relationship [15]

$$E_d = \beta N_c Z_a N_e \quad (4)$$

where N_c is the coordination number of the cations nearest-neighbor to the anion, Z_a is the formal chemical valency of the anion and Ne is the effective number of the valence electron per anion. β = 0.26 ± 0.04 and 0.37 ± 0.05 for ionic and covalent materials, respectively.

For deposited film Sn_2S_3, Z_a and N_e, respectively, take the values 2 and 10. It is well known that in Sn_2S_3 the three sulfur (S) atoms are at shorter distance and the other five at a longer one [13]. The calculated β was approximately 0.22 then indeed, Sn_2S_3 films appear to fall into ionic class.

The relationship between the lattice dielectric constant ε_L, and the squares of refractive index n is given by [16].

$$n^2 = \varepsilon_L - B.\lambda^2 \quad (5)$$

Where ε_L is the lattice high frequency dielectric constant and $B = \frac{e^2}{\pi c^2}\frac{N}{m_e^*}$ was constant. N/m_e^* is the ratio of the free carrier concentration to the electron effective mass., c is the speed of light, and e is the electron charge. Figure. 6 represent the relation between n^2 and λ^2 for Sn_2S_3 thin film. The values of ε_L and N/m_e^* were determined from the intercept of the extrapolating straight line with n^2 axis. The obtained values were 3.55 and 1.3 10^{42} $\mathbf{g}^{-1}$ cm^{-3} for ε_L and N/m_e^*, respectively. The value of the effective mass m_e^* was calculated by using the relation [18]:

$$1/m^* = 1 + p^2/2m\,E_g \quad (6)$$

where E_g is the band gap energy, $m^* = m_e^*/m$, m is the free electron mass and $p = \hbar G$, G being the smallest reciprocal lattice vector. Thus, p is equal to ħ/a where a is the lattice constant. Using the value of E_g and the value of lattice constant (a) was estimated from the XRD measurement [3]. The evaluated effective mass is $m_e^* = 4.32 \times 10^{-31}$ kg ($m^* = 0.476$) . The carrier density N calculated for Sn_2S_3 film was ≈ 5.61×10^{14} cm^{-3}. We notice a certain consistency for concentration N calculated and determined by Hall Effect [3].

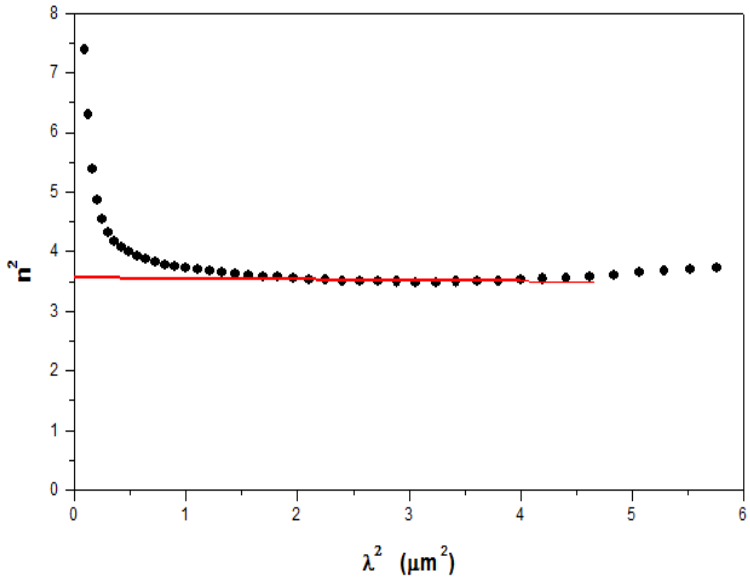

Figure.6. *Plots of n^2 versus λ^2 of Sn_2S_3 thin film.*

The variation of the real part of the dielectric constant ε_1 with incident photon energy depends on the plasma frequency ω_p. When $n^2 >> k^2$ and $\omega\tau << 1$ the dielectric constant ε_1 can be expressed by the relation [6]:

$$\varepsilon_1 = \varepsilon_\infty - [(\varepsilon_\infty\ \omega_P^2)/\omega^2] \quad (7)$$

where τ is the relaxation time and ω the angular frequency of the lattice atoms. Figure.7 represents the relation between ε_1 and ω^{-2} for Sn_2S_3 thin films. The values of plasma frequency ω_p and infinite dielectric constant ε_∞ determined from the slop and intercept of the ε_1 versus ω^{-2} plot were $\omega_p = 0.51 \times 10^{14}$ s^{-1} and $\varepsilon_\infty = 3.51$, respectively. According to M.M.El.-Nahass et al. [17] the disagreement between the values of ε_∞ and ε_L may be due to free carrier contribution.

The dielectric relaxation time was evaluated using the relation [19-20].

$$\tau = \frac{\varepsilon_\infty - \varepsilon_1}{\omega\ \varepsilon_2} \quad (8)$$

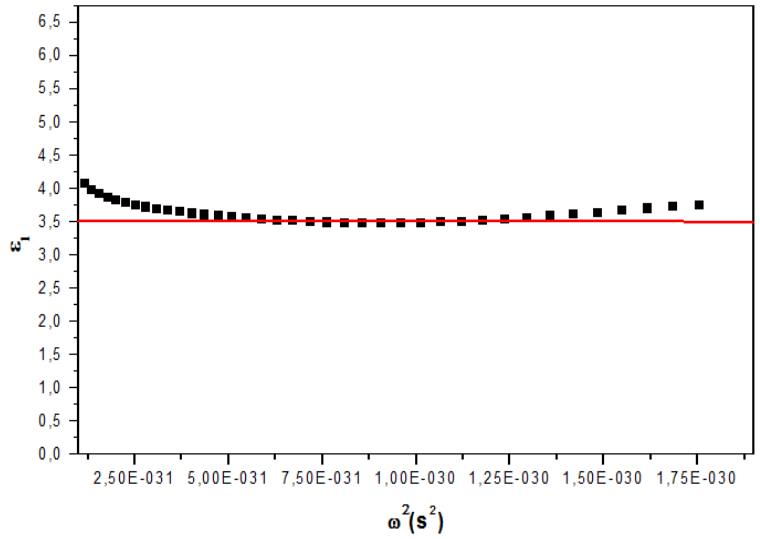

Figure.7. *Plots of ε_1 versus ω^{-2} of Sn_2S_3 thin film.*

Figure. 8 represent the dielectric relaxation time as a function of photon energy for Sn_2S_3 films. The spectrum variation of the dielectric relaxation time has a maximum value located at 0.74 eV. We attribute this maximum to the indirect optical gap transition, which is comparable with the value obtained from the optical absorption measurements.

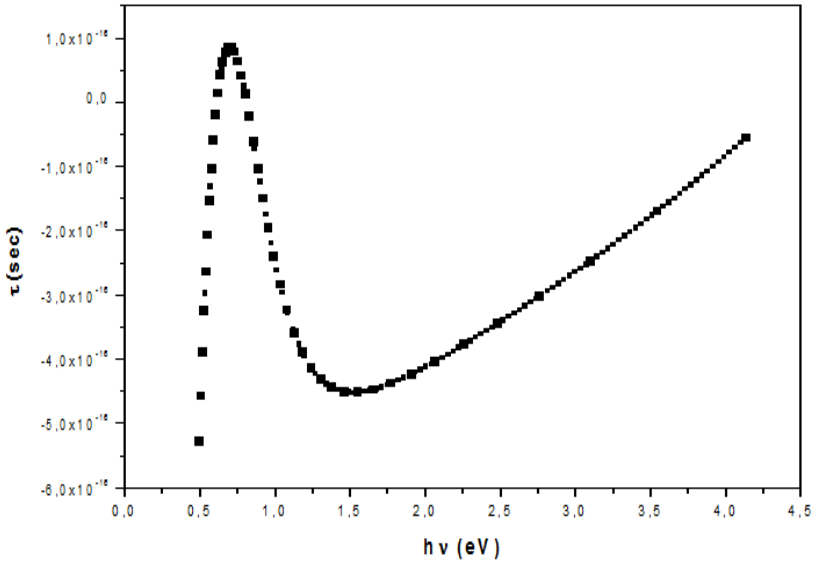

Figure.8. *Plots of τ versus of $h\upsilon$ of Sn_2S_3 thin films*

IV. CONCLUSIONS

Nanocrystalline Sn_2S_3 thin film was prepared on glass substrates by spray pyrolysis technique at the temperature of 270 °C .The pattern search optimization technique was successfully applied to extract the thickness and optical constants. The value of dispersion energy E_d determined by single-oscillator model was found to be 13.5 eV. The calculated value of β showed the ionic nature of Sn_2S_3 thin film. We identified both types of optical transitions

(indirect and direct). The indirect and direct optical gaps values correspond to 0.74 and 2 eV, respectively. The values of dielectric constants, plasma frequency, effective mass and carrier concentration were also calculated.

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